Preparation of Fe_3O_4 Thin Films by a Chemical Bath Technique

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This letter describes a new method to prepare Fe_3O_4 thin films on glass substrates from aqueous solutions kept in a temperature range from 333 to 343 K. The process includes the deposition of precursor thin films, α-FeOOH, by oxidation of Fe^{2+} ion in aqueous solutions, and the conversion of the precursor to Fe_3O_4 in another solution. The film thickness, microstructure and magnetic properties of the resultant Fe_3O_4 thin films were characterized.

Preparation of ceramic thin films in aqueous solutions has attracted much attention. A variety of techniques have been reported.[1] These techniques are based on the formation of metal oxide embryos in aqueous solutions followed by heterogeneous nucleation on the substrates soaked in the solutions. The advantages of such techniques over the conventional alkoxide dip-coating method are that (1) ceramic thin films may be obtained near room temperature or the subsequent heat-treatment temperature may be lowered largely, and (2) ceramic coatings may be formed on small-sized substrates such as fine powders which are difficult to be used in the dip-coating operation. The present authors have prepared SnO_2,[2,3] MnO_2,[4] CeO_2,[4] and Co_3O_4[5] thin films from aqueous solutions at temperatures from 323 to 333 K.

Fe_3O_4 thin films have also been prepared from aqueous solutions by a number of workers. Abe et al.[6] established a so-called "ferrite plating" method in which Fe^{2+} ions in aqueous solutions are oxidized by introducing air or other oxidizing agents in the vicinity of the substrates to promote the formation of Fe_3O_4 on the substrates. Izaki and Shinoura[7] used an electroless plating technique in which Fe^{3+} ion was reduced with dimethylaminoborane to form Fe_3O_4.

In this paper, we describe a new method to prepare Fe_3O_4 thin films consisting of two-step operations; (i) deposition of α-FeOOH precursor thin films in aqueous solutions and (ii) conversion of the precursor films to Fe_3O_4 films in another solution. The effect of the composition of the solutions was investigated and some properties of the resultant Fe_3O_4 thin films were characterized.

The precursor films were prepared in the following manner. $FeSO_4(NH_4)_2SO_4$ and $KClO_3$ were dissolved in 100 cm^3 of deionized water in a polyethylene bottle. The concentrations of Fe^{2+} and $ClO_3{}^-$ were adjusted in the ranges of 1.0 to 10.0 mmol/dm^3 and 2.0 to 20.0 mmol/dm^3, respectively. Glass slides were immersed in the solutions, and the solutions were kept at 333 K for 24 h. The chemical reactions occurring in the solutions were the oxidation of Fe^{2+} to Fe^{3+} (Eq 1) and the subsequent hydrolysis to form α-FeOOH (Eq 2).

$$6Fe^{2+} + ClO_3{}^- + 6H^+ \rightarrow 6Fe^{3+} + Cl^- + 3H_2O, \qquad (1)$$

$$6Fe^{3+} + 12H_2O \rightarrow 6\alpha\text{-}FeOOH + 18H^+. \qquad (2)$$

When the rate of reaction (1) is slow enough for heterogeneous nucleation to predominate, the precursor precipitates predominantly on the surfaces of the glass slides and the inner wall of the bottles.

The precursor was converted to Fe_3O_4 in the following manner. $FeSO_4(NH_4)_2SO_4$ and CH_3COONa were dissolved in deionized water to the concentrations of 0.04 and 3.0 mol/dm^3, respectively. The water had been deaired by passing Ar gas to avoid unnecessary precipitation. Then, α-FeOOH thin films were transferred to the solution, and the solution was kept at 343 K for 2 h.

During this stage, α-FeOOH reacted with Fe^{2+} to form Fe_3O_4 (eqs 3–5).[8]

$$Fe^{2+} + OH^- \rightarrow FeOH^+, \qquad (3)$$

$$2\alpha\text{-}FeOOH + FeOH^+ \rightarrow [FeOOH]_2FeOH^+, \qquad (4)$$

$$[FeOOH]_2FeOH^+ \rightarrow Fe_3O_4 + H_2O + H^+. \qquad (5)$$

In some cases, the resultant Fe_3O_4 films were heat-treated at 673 K for 30 min in a flow of CO.

The films were subjected to X-ray diffraction (XRD) analysis with a Rigaku RINT 2200 diffractometer using Cu Kα radiation, scanning electron microscopic (SEM) observation with a JEOL JSM-6330F microscope, film thickness measurement with a Dektak 3030 surface profilometer, and magnetization behavior with a Model 1660 vibrating sample magnetometer (VSM) of Digital Measurement Systems, Inc.

The optimum concentrations of Fe^{2+} and $ClO_3{}^-$ were set to be 5.0 and 10.0 mmol/dm^3, respectively, because smooth and strongly adherent thin films were obtained with good reproducibility. Further experiments were made on the films prepared under this condition.

Figure 1 shows the XRD profiles of the precursor and Fe_3O_4 thin films prepared in the present work. Although the crystallinity of the former is quite low, the diffraction profiles were con-

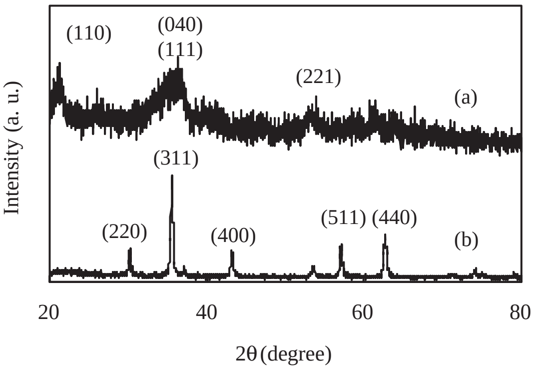

Figure 1. X-ray diffraction profiles of (a) precursor and (b) Fe_3O_4 thin films.

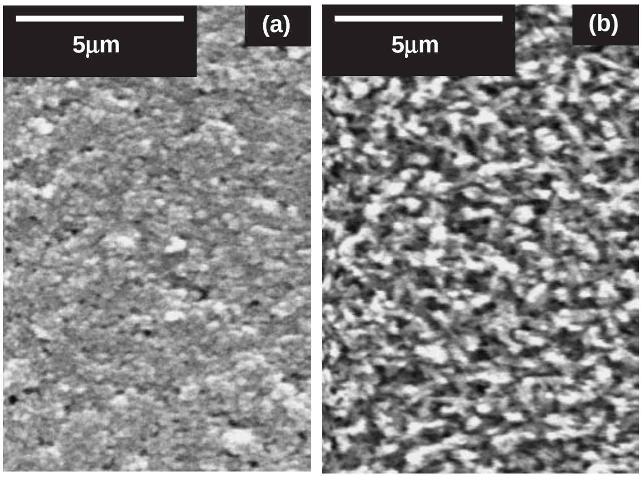

Figure 2. SEM photographs of (a) precursor and (b) as-prepared Fe_3O_4 thin films.

sistent with those listed in JCPDS Cards Nos. 29-713 and 19-629, respectively.

The thickness of an α-FeOOH thin film deposited for 24 h was about 600 nm, and it slightly decreased upon being converted to Fe_3O_4 to 580 nm. It is noteworthy that the film thickness was quite homogeneous over the whole film area. Although dip-coated thin films often have thicker area near the ends of the substrates, such inhomogeneity in film thickness was not observed in the films prepared by the present method. The precursor and Fe_3O_4 films were composed of small particles about 100 nm in diameter as shown in Figure 2. The Fe_3O_4 film was found to be porous.

The adhesion of α-FeOOH thin films to the substrate was very high, while that of Fe_3O_4 was not so high and the films were detached off the substrate when they were mechanically scraped. However, the adhesion of Fe_3O_4 thin films was greatly improved by a heat-treatment in CO at 673 K.

Figure 3 shows the magnetization curves of as-deposited and heat-treated Fe_3O_4 thin films. Both films show ferrimagnetic behavior. A heat-treatment in CO at 673 K largely increased the coercivity.

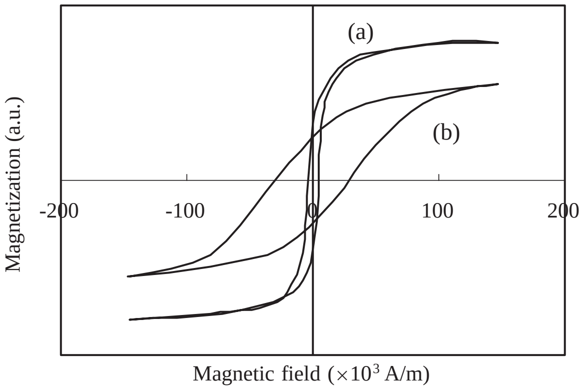

Figure 3. Magnetization curves of (a) as-deposited and (b) heat-treated Fe_3O_4 thin films.

In summary, Fe_3O_4 thin films were prepared in aqueous solutions by a two-step process; deposition of α-FeOOH precursor thin films at 333 K and the conversion to Fe_3O_4 at 343 K. The optimum preparation condition has been established. The resultant Fe_3O_4 thin films showed ferrimagnetic behavior, and the coercivity was increased by a heat-treatment at 673 K in CO.

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